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AFRPL-71-85



QUARTERLY PROGRESS REPORT THERMALLY STABLE BURNING RATE ACCELERATORS (U)

Contract F04611-70-C-0066

JULY 1971

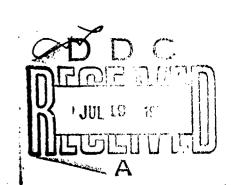
Prepared for
Air Force Systems Command
Air Force Propulsion Laboratory
Edwards Air Force Base, California 93523

Prepared by

Thickol HUNTSVILLE DIVISION

Huntsville, Alabama

A DIVISION OF THIOKOL CHEMICAL CORPORATION



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FOREWORD

This report is prepared in accordance with the requirements of Contract F04611-70-C-0066.

Program Structure Number 623148
Program Number 3148
Program Element Number 6.23.02F

Program Monitors Capt C.L. Ennis and

l/Lt D. J. Yardley

USAF/RPMPC

Prime Contractor Thiokol Chemical Corporation

Huntsville Division Huntsville, Alabama

This report, the fourth quarterly progress report to be issued under this program, covers effort performed for the period 1 March through 31 May 1971. This report has been assigned the Thiokol internal number 26-71 (Control No. C-71-26A).

The principal investigators on the program are Dr. W. D. Stephens, Dr. D. A. Flanigan, and Mr. J. O. Hightower. Dr. M. Miller is serving as Program Manager. In addition to those contributions by the principal investigators, major contributions to the program were made by Dr. T. C. Willis, Messrs. J. W. Blanks, C. M. Christian, Mrs. Patricia B. Walters, and Dr. R. E. Rogers. The over-all Project Director is Mr. G. F. Mangum.

STATEMENT OF APPROVAL

Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange of ideas.

G. F. Mangum, Project Director

ABSTRACT

A six-pound sample of thermally stable ammonium perchlorate has been prepared and small particle size AP produced by freeze-drying, fluid energy milling, and solvent/non-solvent precipitation techniques. The freeze drying process produced 0.73 micron oxidizer with a thermal stability of 54 hours to 1% weight loss at 375°F. The fluid energy mill produced 4.6 micron oxidizer with a stability of 35 hours. Particle size was larger than desired, and moisture (the critical impurity) was higher than expected. The solvent/non-solvent precipitation produced 1.03 micron oxidizer with a stability of 175 hours. All methods appeared attractive even though the product from the fluid energy mill was below expectations (and previously demonstrated size and quality) in these limited tests.

Thermal stability of ferrocene-type catalysts has been related to certain classes of impurities and to specific features of molecular design. Compounds with electron-withdrawing groups and those without alpha hydrogen atoms have shown improved resistance to thermal and oxidative attack. In addition, insoluble ferrocene compounds appear much more stable in propellant, probably because of decreased contact with other ingredients.

Interrelationships between AP stability, AP particle size, and catalyst type have been studied in propellant. The most stable propellants appear to be those which have insoluble catalysts and large AP particles.

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INTRODUCTION

- (C) The purpose of this program is to research the methods and materials that will produce thermally stable AP and burning rate catalyst. They will be used with other thermally stable propellant ingredients to produce a solid propellant that is capable of withstanding a temperature environment of -75° to 350°F.
- (C) With the present capability of aircraft to fly at supersonic speeds, a new requirement now exists for missiles which can be carried externally. The major development problem arises from the effects of aerodynamic heating, causing missile skin temperatures of several hundred degrees Fahrenheit. In addition, the external carry means that a missile in the airstream is exposed to temperatures of about -65°F (the temperature in the isothermal layer). Missiles and missile components therefore are subject to temperatures from -65°F to well over 300°F.
- (C) Propellants that will survive this treatment, and also possess the desirable ballistic properties, are not available. Two general approaches to assure the rocket motor's operation at all times are to insulate the motor or develop a propellant to withstand the environment. Internal or external insulations increase the motor cross sectional area and weight. Also, internal insulation decreases propellant volume. Since the missile is normally exposed to these conditions for a relatively short time, the insulation approach is inefficient. The penalties paid for insulation are too great; thermally stable propellant is a better solution.

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PROGRAM OBJECTIVES AND ORGANIZATION

OBJECTIVES:

(C) Very small particle exidizer (less than one micron) and burning rate catalysts have been used to achieve high burning rates; however, commercially available ammonium perchlorate is prone to thermal decomposition which, in turn, degrades propellant. Some liquid burning rate catalysts also have undesirable characteristics such as crystallisation, migration, or volatilization and are subject to thermal and exidative decomposition. The objectives of this program are: (1) to develop methods of production of stable ultrafine ammonium perchlorate (UFAP), (2) to demonstrate improved methods of burning rate catalysis, and (3) utilization of these rate augmentation techniques in propellants which must survive temperature cycling up to 350°F.

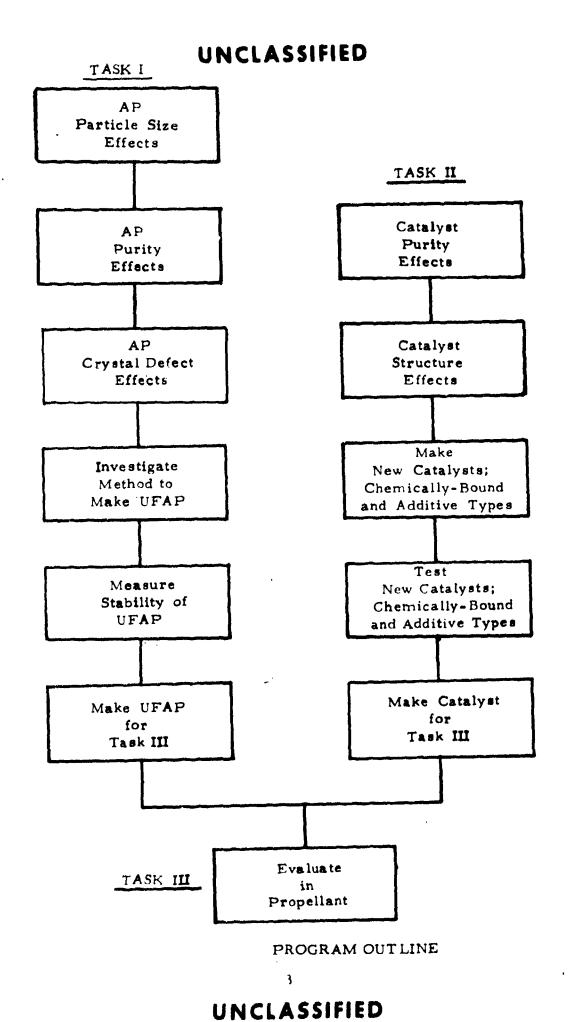
PROGRAM ORGANIZATION:

(U) This program is divided into three tasks as follows:

Task I, Thermally Stable UFAP, is subdivided into three subtasks. The first defines AP thermal stability and identifies the qualities that AP must have to be stable. In the second, new methods of preparing UFAP are examined and in the third subtask, the method of preparing UFAP is chosen and enough UFAP prepared for the demonstration part of the program.

Task II, Thermally Stable Catalysts, is divided into four subtasks. These include impurity investigations, structure investigations, improved catalysts, and synthesis of material for Task III.

Task III, Demonstration, is that part of the program in which the thermally stable UFAP and an improved catalyst are combined into a propellant for demonstration.



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ACCOMPLISHMENTS

Task 1 - Thermally Stable Ammonium Perchlorate

A six pound sample of thermally stable ammonium perchlorate was prepared by recrystallization from distilled-deionized water followed by shock precipitation out of water with cold isopropyl alcohol. This sample exhibited a thermal stability (time to 1% weight loss at 375°F) of 19.7 hours. Exposure of the sample to a vacuum drying process (60 hours at 145°F under a 10 micron vacuum) improved the thermal stability to 53 hours (Figure 1). The sample exhibited a weight median diameter of 38 microns. Portions of this six-pound sample of thermally stable ammonium perchlorate have been reduced in size through spray freeze drying, fluid energy milling, and solvent/non-solvent precipitation.

Spray Freeze Drying

A 200-gram sample of spray freeze dried ammonium perchlorate was obtained by spraying a water solution of the oxidizer into a trichloro-ethylene freezing medium. No coating agent was included in this experiment. Following sublimation of the water from the frozen cake, the resultant particle size was 0.86 microns. The thermal stability, as measured in isothermal TGA at 375°F, was 67 hours. A similar spray freeze dry experiment was performed except that 1% Strodex PK90 was included as a coating agent for the oxidizer. Following sublimation, the sample exhibited a particle size of 0.73 microns. The thermal stability measured at 375°F was 54 hours, essentially the same thermal stability as was noted on material from which the spray freeze dried oxidizer was obtained.

Fluid Energy Milling

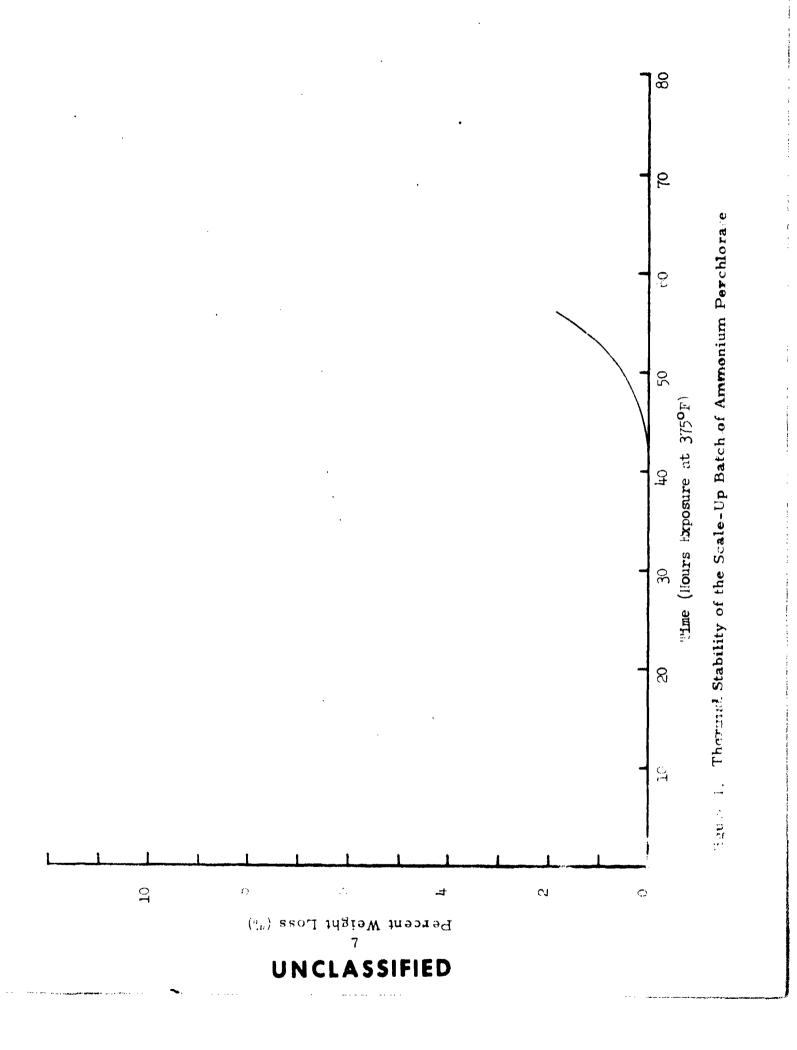
Another sample of the thermally stable AP was reduced in particle size on a Trost mill (small fluid energy mill). Although particle reduction was not as low as expected (4.6 microns in two passes through the mill), it is expected that with either a greater number of passes or a larger mill, a further reduction in particle size can be readily obtained. The moisture content of the oxidizer prepared in this manner was excessive and a severe agglomeration of the oxidizer occurred. The moisture content was reflected in a relatively poor thermal stability at 375° F (35 hours to 1% weight loss). This sample of oxidizer was dried at elevated temperatures in a vacuum open and re-examined as to its thermal stability after this treatment was completed. The sample did not exhibit improved thermal stability following the drying process even though initial weight losses andicated that substantial quantities of volatiles had been removed. No explanation is readily available for the failure of this material to exhibit higher thermal stability.

Solvent/Non-solvent Recrystallization

Another sample of AP was reduced in particle size by a solvent/
non-solvent precipitation technique. The technique was to dissolve the
prepurified thermally stable AP in methanol and precipitate the oxidizer
through addition of the methanol-oxidizer solution into chlorobenzene. The
resultant particle size was 1.03 microns. The thermal stability test at
375°F was terminated at 73 hours with less than 1% weight loss. The projected 1% weight loss time would be greater than 100 hours. The sample
prepared from solvent/non-solvent precipitation was extensively dried and
still exhibited an initial weight loss although the amount of that weight loss
was approximately 50% of that noted before the drying. The thermal stability
was somewhat improved over that previously observed in that a projected
time to 1% weight loss was 175 hours.

The results of these data indicate that particle size reduction of AP can be achieved through a wide variety of techniques. Except when the moisture content of the AP was high, the thermal stability of the AP was improved over that of the basic (purified) starting material.

Effort is presently underway to carefully dry HTPB polymer, IPDI and DDI isocyanate curing agents, powdered aluminum and sub-micron AP prepared from fluid energy milling and solvent/non-solvent precipitation, in order that a series of 10-gram mixes can be manufactured to determine what percent UFAP can be incorporated into a propellant without seriously degrading thermal stability. Propellants will also be manufactured with polyferrocenyl methylene in order to determine what percentage of this catalyst can be tolerated without degradation in thermal stability. These mixes will be manufactured in 10-gram quantities and cast into cube form samples from which isothermal TGA data will be obtained. Larger mixes, and samples, will subsequently be prepared for evaluation of tensile, ballistic and aging characteristics.



TASK II - THERMALLY STABLE CATALYSTS

The technical approach to achieving thermally stable burning rate catalysts was initiated with a study of the impurities present in alkyl ferrocenes, and the effects of these impurities upon propellant stability. These experiments showed that three critical classes of impurities had to be eliminated to improve thermal stability. These classes are the hexane insoluble components, the volatile materials, and the ionic contaminants. The second part of Task II involves an assessment of those features of molecular structure which contribute most to the oxidative and thermal stability of ferrocene compounds. Three important aspects of molecular design have been derived from these researches. Catalysts which are to be thermally stable and oxidatively resistant should contain electron withdrawing groups, should have no alpha-hydrogen atoms, and should be insoluble in the propellant binder system.

Synthesis of Model Compounds

Synthesis of model compounds is essentially complete as described in the previous quarterly report. During this period two new materials have been synthesized and evaluated. These include polyferrocenyl methylene, prepared by zinc chloride polymerization of hydroxymethyl ferrocene as shown below:

Benzoylation of benzoylferrocene with benzoylchloride in aluminum chloride gave a 30% yield of dibenzoylferrocene.

Oxidation Susceptibility Tests

Throughout this program the reaction of model ferrocene compounds with air at slightly elevated temperatures has been used as a criterion of oxidation susceptibility. Significant progress has been made in finding model structures which are more resistant to oxidation than the standard compound n-butylferrocene. Six of the models tested show significant improvements in oxidative resistance by comparison. The rate of air up-take for several of these compounds is shown in Figure 2. Polyferrocenylmethylene, an insoluble compound, and dibenzoylferrocene also an insoluble compound, show no measurable reaction with oxygen under the experimental conditions.

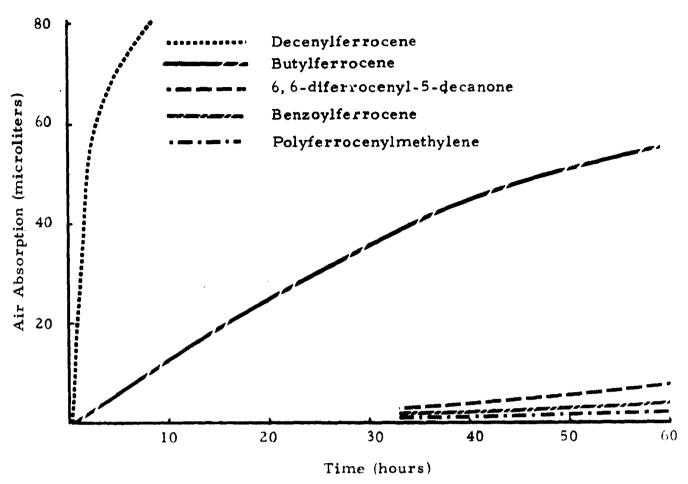


Figure 2. Air Uptake at 90°C.

The net result of these model studies with regard to oxidation resistance at elevated temperature is to indicate that electron withdrawing groups, absence of alpha-hydrogen atoms, or use of insoluble ferrocene compounds will provide best thermo-oxidative stability.

Evaluation of Models in Propellant

In order to examine the effect of catalyst models of different structural types upon the thermal stability of propellant, small propellant samples were made using a suboxy terminated polybutadiene binder cured with an epoxide

The propellants contained 50% standard grind oxidizer and 10% H-30 aluminum. One-half gram samples of cured propellant were diced into small cubes, and analyzed by TGA. These experiments were designed to be an extreme test of propellant stability, in order to screen the various models. Dicing the propellant allowed a large surface area exposure and easier loss of volatile decomposition products. In general, the results of stability tests in propellant correlated very well with the air oxidation susceptibility tests on pure catalysts. The TGA weight loss curves shown in Figure 3 indicate a significant improvement in the thermal stability of propellant as measured by TGA, through the use of appropriate catalyst models. The insoluble models, those containing electron withdrawing groups, and those in which alpha-hydrogen atoms are absent, present the most improved structures, as in the air-uptake tests.

A qualitative correlation of oxidation resistance of model catalysts and thermal stability of propellants is shown in Table I. In general, the oxidation resistance and propellant data are in good agreement. (Small numerical rating indicates good stability.)

TABLE I

RANKING OF MODEL CATAYLSTS BY AIR ABSORPTION

AND BY TGA ON PROPELLANTS

Model	Stal	bility
#Accessing the Control of the Contro	Air	TGA
Polyferrocenylmethylene	1	1
Dibenzoylferrocene	2	2
Benzoylferrocene	3	4
6, 6-Diferrocenyl-5-decanone	4	5
2-Ferrocenyl-2-methyl-3-pentadecanone	5	8
Decanovlferrocene	6	7
n-Butylferrocene	7	9
l-Acetyl-l ^l -decanoylferrocene	8	10
Tridecylferrocene	9	6
Decylferrocene	10	11
Decenylferrocene	11	3

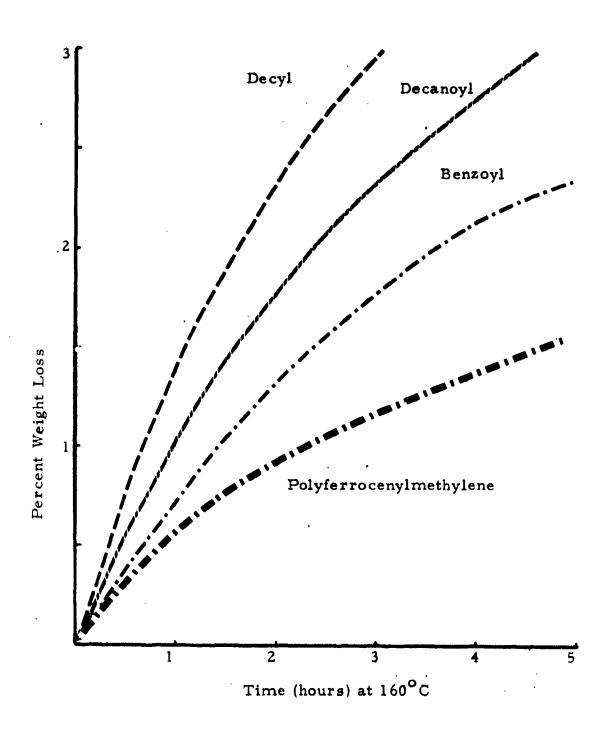


Figure 3. TGA Tests of Catalyzed Propellants

In the early TGA experiments done with propellant, it was not clear whether weight loss was due primarily to catalyst loss by evaporation or to chemical interaction producing other volatile components. In order to examine this possibility, propellants were made in which the oxidizer was replaced by sand and by aluminum. Essentially no weight loss occurred when these propellants were analyzed by TGA.

Oxidizer-Catalyst Interactions

All of the propellant work which had been done up to this point in the program had been done utilizing standard high speed grind oxidizer which was ~ 20 micron in particle size and had a thermal stability of approximately three hours to 1% weight loss at 190°C. It was felt that a better test of propellant stability could be realized if oxidizer which had been purified and rendered stable by the purification technique described in Task I was used to make propellant. Accordingly, a sample of very stable oxidizer (100 hours to 1% weight loss by TGA at 190°C) was used in the same propellant and weight loss was measured by TGA. The thermal stability of propellant made using this oxidizer was considerably less than had been anticipated, however, particle size of this oxidizer sample was approximately two microns, much finer than the 20 micron oxidizer used in the previous test. It appeared that the interaction between particle size and oxidizer stability might be more complex than anticipated, and as a result a third propellant was made using approximately 15 micron oxidizer with 18 hour stability. A significant improvement in propellant stability was noted as a result. The data from these experiments is shown below:

AP	10 t		Propellant TGA, 160°C			
Time to 1% Wt. Loss, 190°C	Particle Size	4 Hrs.	% Wt. 8 Hrs.	Loss in 12 Hrs.	14 Hrs.	
3 hours	20	2.1	3.4	4.5	4.8	
18 hours	15	2.2	2.8	3.1	3.2	
100 hours	2	4.0	5.3	6.6	7.2	

Propellants made to investigate this point were formulated using carboxy terminated polybutadiene and an epoxide cure as were previous propellants. However, benzoylferrocene was used as the ferrocene type catalyst as a matter of convenience, and because of the relatively good stability exhibited previously.

Thermal Stability, Particle Size, and Catalyst Type

The results of the experiment just described suggested that a more detailed approach was required to investigate interactions between propellant thermal stability, AP thermal stability, AP particle size and type of ferrocene catalyst (primarily soluble versus insoluble catalyst). An experiment was planned and executed in order to investigate these interrelationships. Three variables were investigated. These included oxidizer particle size, oxidizer stability, and catalyst solubility. In order to perform this experiment it was necessary to obtain the following four samples of ammonium perchlorate; two which would be fine oxidizer and two which would be large oxidizer. The fine oxidizer was required as a stable material (as judged by TGA on pure oxidizer) and as an unstable material, and the large oxidizer likewise was required as a stable sample and as an unstable sample. Ideally, the particle size of the stable and unstable samples would be the same and a divergence in stability would be quite large. However, not all of the specific particle sizes and stabilities were available, and compromises were made in order to perform the experiment. The four oxidizer samples were run in propellants with benzoyl ferrocene representing a soluble catalyst, and polyferrocenylmethylene representing an insoluble catalyst. This made a total of eight propellants under evaluation. In contrast to earlier propellants made for stability studies, a change was made in the program at this point to incorporate HTPB as the primary binder under investigation. As a result, all of these propellants were made with R-45M, hydroxy terminated polybutadiene, cured with DDI curing agent.

Because a large number of variables were incorporated in this experiment, it is felt necessary to present a history of the oxidizer used. large stable oxidizer had a weight median diameter of 46 microns as measured by the MSA analysis. The material had been recrystallized rapidly from water, and then precipitated by pouring a hot aqueous solution seeded with Alon T into cold isopropyl alcohol. The product had been vacuum dried at 60°C for 60 hours, and TGA showed time to 1% weight loss at 195°C to be 53.7 hours. The large unstable oxidizer was commercial material described as "50 micron round" particles and had a TGA stability of 3 hours to 1% weight loss. The fine stable oxidizer was fluid energy milled oxidizer which contained TCP, and had been stored in a refrigerator. The thermal stability showed 100 hours to 1% weight loss and a particle size of 2.3 microns was measured by MSA analysis. The fine unstable oxidizer was recrystallized rapidly from ultra-pure water, precipitated rapidly by pouring methyl alcohol solution into cold chloroform. The product was vacuum dried at 60°C for 30 hours. The TGA showed time to 1% weight loss at 195°C to be 3.3 hours, and the MSA particle size analysis showed 7.2 microns.

No attempt was made to control surface area of the oxidizer, and once again, 1/2 gram samples of propellant were diced into small cubes and the sample analyzed by TGA. A summary of TGA data on the individual propellants is shown below.

AP	Particle Size	Stability 1	Wt. Loss in 5 hour	s at 160°C
	(micron)	(hours)	Benzoylferrocene	Polyferrocenyl- methylene
Fine, Stable	2.3	100	4.58%	3.19%
Fine, Unstable	7, 2	3	3.03%	2.05%
Large, Stable	46	53	0.57%	0.43%
Large Unstable	50	3	1.34%	0.93%

Stability of AP is reported as the time to 1% weight loss at 195 $^{
m o}$ C.

Interaction Data Analysis

The data from the above experiments were analyzed by comparing the average weight losses of groups of propellants. The analyses are outlined below:

Α.	Variables Considered Singly	% 0	Δ
	1. Fine AP average	3,21	
	Large AP average	0.82	2.39
	2. Soluble catalyst average	2,38	
	Insoluble catalyst average	1.65	0.73
	3. Stable AP average	2.19	
	Unstable AP average	1.85	0.35

B. Variables Considered Two At A Time

1. Catalyst and Particle Size		
a. Soluble, large	0.96	
Soluble, fine	. 3.80	2.84
b. Insoluble, large	0.68	
Insoluble, fine	2.62	1.94
c. Soluble, large	0.96	
Insoluble, large	0.68	0.28
d. Soluble, fine	3.80	
Insoluble, fine	2.62	1.18
2. Catalyst and AP Stability		
a. Soluble, stable	2.58	
Soluble, unstable	2.19	0.39
b. Insoluble, stable	1.81	
Insoluble, unstable	1.49	0.32
c. Soluble, stable	2.58	
Insoluble, stable	1.81	0.77
d. Soluble, unstable	2.19	
Insoluble, unstable	1.49	0.70
3. AP Stability and AP Particle Size		
a. Stable, fine	3.89	
Stable, large	0.50	3.39
b. Unstable, fine	2.54	
Unstable, large	1.14	1.40
c. Stable, fine	3.89	
Unstable, fine	2.54	1.35
d. Stable, large	0.50	
Unstable, large	1.14	0.64

C. Variable Considered Three At A Time

The values for this set are the same as those reported in Table II.

CONCLUSIONS:

Fine AP is more detrimental to catalyzed propellant stability than large AP. This is true for both stable and unstable oxidizer. In addition, insoluble catalysts give more stable propellant than soluble catalysts. The effect of catalyst solubility is more pronounced with fine AP than with large AP. AP stability (as determined by TGA) or pure AP samples is less important in catalyzed propellant than AP particle size. The greatest stability in propellant resulting from these experiments is obtained using large particle, stable oxidizer and an insoluble catalyst.

A possible anomaly exists in the unusual results in Part A-3 of the Interaction Data Analysis; consequently, an erroneous conclusion would be that unstable AP makes better propellant than stable AP. However, that conclusion would change drastically if the results from the fine-unstable oxidizer were higher than the results from the fine-stable oxidizer. This inversion would probably occur if 2.5-micron unstable oxidizer were used. In other words, the particle size (or surface area) of the fine-unstable sample is not directly omparable to the particle size of the fine-stable sample.

Uncatalyzed Propellant

The lack of correlation between AP stability and propellant stability seen in the previous experiment was unexpected, and it was decided to investigate this point further. The four oxidizer samples described above were used in propellants of the same formulation except that no catalyst was added. The propellant stability was significantly better than that for catalyzed propellant and consequently the comparison temperature was increased to 198°C in order to obtain significant results. Results are shown in Table III. The TGA data was analyzed at 5 hours and again at 12 hours.

TABLE III

AP	Percent Wt. Loss at 198°C			
	5 hours	12 hours		
Fine-stable	0.66	2.6		
Fine-unstable	1.7	3.19		
Large-stable	0.19	0.97		
Large-unstable	0.68	5.86		

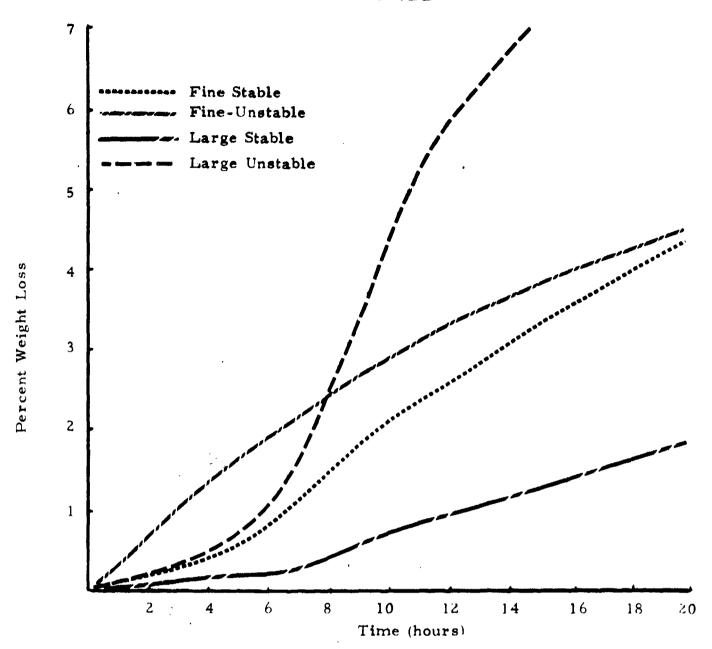


Figure 4. Weight Loss at 198°C, Uncatalyzed Propellant

Conclusions arrived at by analyzing the 5-hour data may vary slightly from conclusions arrived at by using the 12-hour point. An analysis of the data after 5 hours indicates that propellants made with large stable oxidizer are more stable than those made with any other type of AP. The worst condition appears to be that in which fine particle oxidizer is used. The fine stable oxidizer is approximately equivalent to the large unstable oxidizer. Therefore, in uncatalyzed propellants, if fine oxidizer is used, stabilizing the oxidizer is a requirement. In the uncatalyzed propellant data, analyzed on the basis of the 5-hour weight lost, there is a good correlation between stability of the ammonium perchlorate and stability of the propellant.

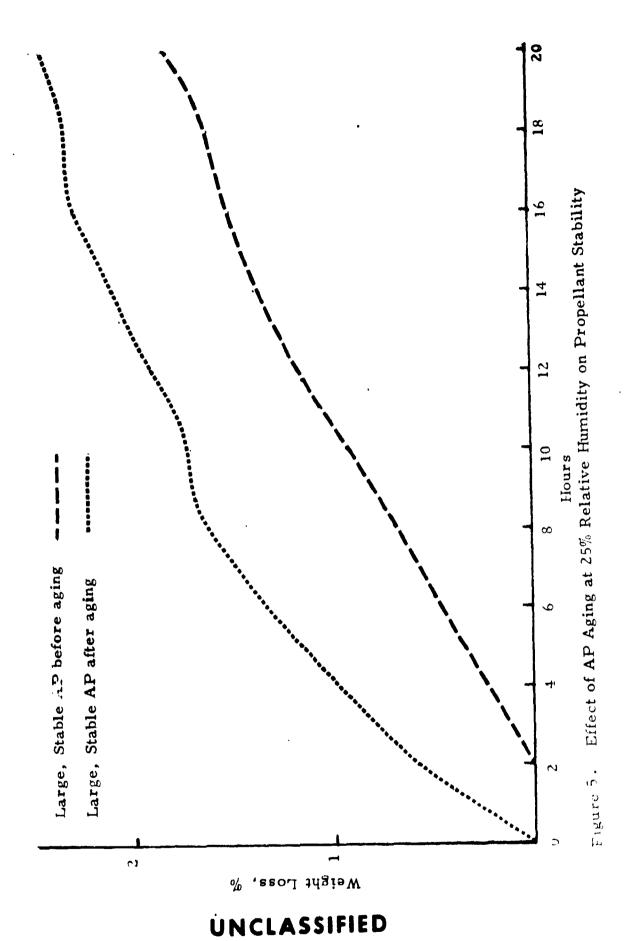
The analysis of the 12-hour weight loss data gives slightly different results. The large stable oxidizer gives the most stable propellant; however, there are slight inversions in the order because of an inverted curve which appears after about 8 hours (see Figure 4).

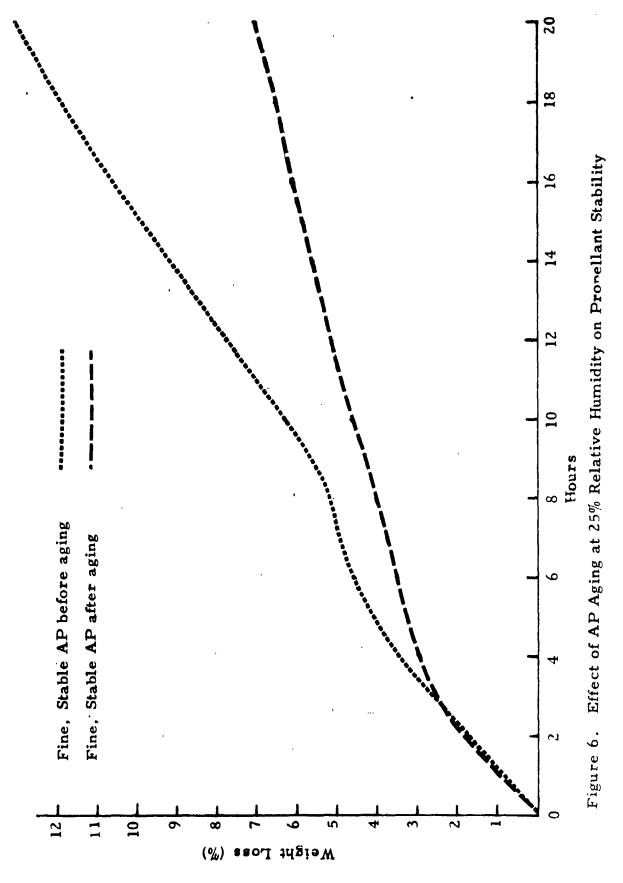
A casual review of the data from these experiments might indicate that unstable oxidizer gives better propellant than stable oxidizer. However, several other factors must be considered. For instance, in a catalyzed propellant the surface condition or surface area of the oxidizer may be more important parameters than particle size. In order to investigate the possibility that surface condition may have a profound influence upon catalyzed propellant stability, two samples of oxidizer were aged in a 25% relative humidity chamber for 70 hours at ambient temperature. It was felt that this treatment might anneal surface defects and improve the stability of ferrocene catalyzed propellant. The results are shown in Figures 5 and 6. Aging of the fine, stable AP gave improved stability in propellant containing benzoylferrocene while the opposite effect was noted for the large stable oxidizer; however, in this instance, the change was much smaller. The results may be due to a change in particle size during aging. This possibility is currently being investigated.

SUMMARY OF THE TASK II EFFORT

As a result of the investigations under sub-task I of this part of the work, three general classes of impurities have been found in ferrocene compounds which seriously aggravate conditions of thermal stability. These classes of coumpounds are the volatile materials, the ionic impurities, and the hexane insoluble components. It has been shown that removal of these classes of impurities by ion exchange resins and precipitation substantially improves the stability of catalysts and propellants with regard to thermal exposure, and oxidative attack.

As a result of the efforts expended in sub-task 2 of this program, cortain features of molecular design have been revealed which will lead to improved ferrocene catalysts for thermally stable propellants. The important conclusions from this work are that alpha-hydrogen atoms should be eliminated, that electron withdrawal groups such as acyl or aroyl should be used, and that insoluble compounds have much improved thermal behavior because of limited contact between catalysts and other reactive components in propellant. With this information in hand, further effort in the program will be directed towards obtaining improved ferrocene catalysts incorporating the features of molecular design which resulted from the previous studies. In addition, further investigations into the interaction between catalyst and oxidizer will be pursued. Specifically, questions relating to amount of catalyst versus thermal stability, and amount of fine oxidizer versus thermal stability will be investigated as discussed under Task I.





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Security Classification			•
DOCUMEN (Security classification of title, body of abstract and	T CONTROL DATA - R&D	the overall report is clessified)	
Thiokol Chemical Corporation		CONFIDENTIAL	
Huntsville Division	25 GRO	J.	
Huntsville, Alabama		iv	
3 REPORT TITLE			
Quarterly Progress Report, The 1 March through 31 May 197	-	Rate Accelerators	
4 DESCRIPTIVE NOTES (Type of report and inclusive dat Quarterly Progress Report, 1		971	
5 AUTHOR(S) (Last name, first name, initial)			
Flanigan, D. A. Stephens, W. D.			
6 REPORT DATE	74- TOTAL NO. OF PAGES	76. NO. OF REFS	
July 1971	31	None	l
F04611-70-C-0066 b project no. 3148	26-71, Control	·	
с	Sb. OTHER REPORT NO(5) (Ar	y other numbers that may be assigned	
d	AFRPL-TR-	71-85	
met, this document is subject to s foreign governments or foreign na	-	nd each transmittal to	TINFO
11 SUPPLEMENTARY NOTES	12. SPONSORING MILITARY AC	TIVITY e Systems Command	
		Air Force Base, Cal.	
A small particle size AP has b	een produced by freeze-	drying, fluid energy	

A small particle size AP has been produced by freeze-drying, fluid energy milling, and solvent/nonsolvent precipitation techniques from a master batch of thermally stable AP. A thermal stability (1% wt. loss at 375 F) in excess of 175 hours has been demonstrated.

The inter-relationships between AP stability, AP particle size, and catalyst type have been studied in propellant.

Ferrocene-type compounds containing electron withdrawing groups and those that do not contain an alpha hydrogen atom exhibited improved thermal stability when compared with n-butylferrocene. Propellants containing ferrocene type catalysts, which are insoluble in the binder, have thermal stabilities that are better than those obtained with counterpart soluble catalysts.

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Burning Rate Accelerators						
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Catalyst purity effects	1					
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INSTRUCTIONS

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